II. General System Description and Extraction Operations, September 1 to November 12, 1993

General Description of the TFF Site

TFF was originally designed to remediate soil and ground water by a combination of soil venting and conventional pump-and-treat technology. Some components were added or modified to accommodate the DUSDP, but the facility remains, basically, a combination of a ground water treatment system and a vapor removal and treatment system. These two systems are briefly described below.

The ground water treatment system (Fig. 2) consists of five components: (1) extraction wells and pneumatic pumps, (2) an ambient-air heat exchanger, (3) oil/water separators (OWS), (4) a UV/oxidation system, and (5) air stripping tanks with granulated activated charcoal (GAC) treatment. Each of these systems are briefly described below.

Ground water is pumped at about 190 liters per minute (L/min, 50 gpm) from three centrally located extraction wells (GEW808, GEW816, and GSW16) with three air lift pumps. These pumps were chosen because of potentially explosive downhole conditions and to minimize emulsification of contaminant in ground water. The combined maximum yield from the pumps, located 42 m (138 ft) below ground surface, is about 230 L/min (60 gpm). Extracted ground water is cooled, from a range of 90° to 93°C (195° to 200°F) to about 38° to 40°C (100° to 110°F), with an ambient-air heat exchanger to prevent thermal degradation of the treatment facility's equipment. Water is then routed to an OWS to remove free-phase gasoline. Even though free product was observed in monitoring wells historically, only about 700 L (180 gals) of free product out of a total recovered gasoline volume of about 26,000 L (7,000 gals) were skimmed from ground water early in the DUSDP. No free product has been recovered directly from extracted ground water since March 1993.

The TFF water treatment system includes a Peroxidation Systems, Inc., model LBV-60, 60 kW UV light/hydrogen peroxide (H_2O_2) oxidation system. Although UV/oxidation can be cost-effective, we experienced reduced hydrocarbon destruction efficiency with the system during and immediately after the DUSDP steam injection. We hypothesize that UV light absorption by aqueous inorganic compounds may have reduced available UV light. In order to deal with some of the single-bonded carbon VOCs, such as chloroform, carbon tetrachloride, and ethylene dibromide, which are poorly degraded in the UV/oxidation process, and to achieve regulatory discharge standards in treated water, a final air stripping process is utilized. After this use, the gas used in the air stripping process is routed through GAC. This treated air then meets BAAQMD requirements of a maximum 10 parts per million by volume (ppmv) total hydrocarbon concentration.

Although TFF was designed to meet National Pollutant Discharge Elimination System (NPDES) requirements, trace levels of some VOCs and some inorganic compounds in the treated
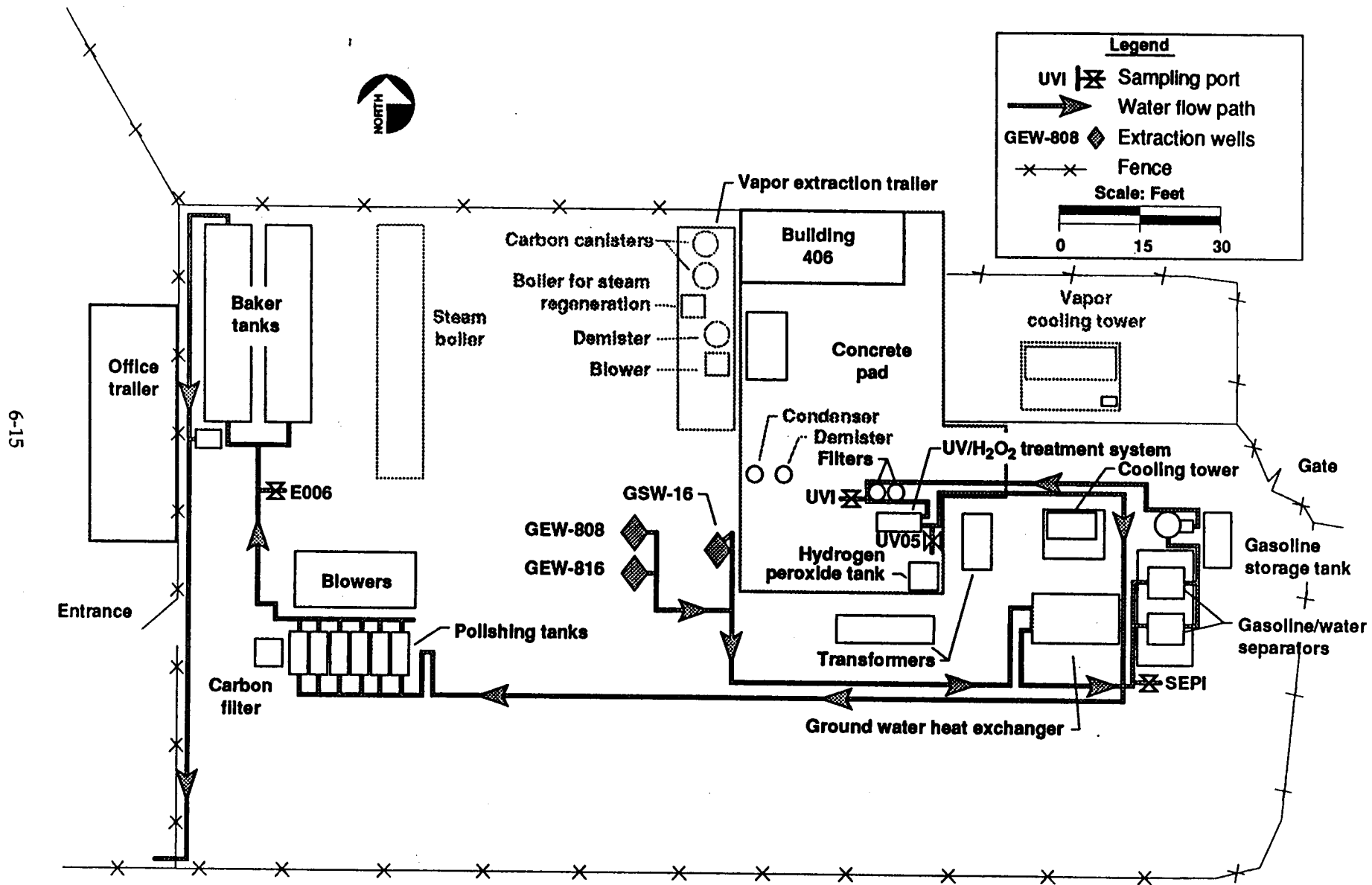
Figure 2. TFF water treatment system.

effluent were detected at slightly elevated concentrations during the DUSDP. In order to proceed with the DUSDP, permits were obtained to discharge treated water to the sanitary sewer. Because these permits were still in effect during the ARV project, we continued to exercise this option.

The vapor treatment system at TFF (Fig. 3) consists of (1) extraction wells, (2) a flat plate heat exchanger, (3) a condensate treatment system, (4) an internal combustion engine system for hydrocarbon destruction, and (5) an activated charcoal adsorption system. Each of these system components is briefly described below.

The vapor treatment system extracts vapor primarily from the same three centrally located extraction wells as the ground water treatment system. These wells are screened in the vadose zone, beginning about 20 ft below the ground surface. Extraction vacuum is provided by the VR Systems ICE, described below. In addition, we also used the DUSDP steam injection wells, which surround the central extraction wells in a six-spot pattern (the GIW wells of Fig. 1), as supplemental vapor extraction points during the course of the ARV phase of remediation.

During and after the DUSDP, extracted vapor temperatures rose as high as 90°C (195°F). In order to safely handle this vapor, it is first cooled in a flat-plate heat exchanger. Steam (which comprised up to 90% of the extracted vapor during DUSDP) and gasoline are condensed into liquid in the heat exchanger. Thus, two process streams leave the heat exchanger; cooled vapor and condensed fluid. Condensed water and gasoline are pumped to a 20-gpm Megator OWS. Gasoline is skimmed and the remaining water is pumped into the ground water treatment system just upstream of the UV/oxidation system. The condensed fluid is free of particles and microbes, both of which can foul conventionally operated OWSs. The maximum gasoline skimming rate from this unit was about 90 L (24 gals) of gasoline per day during the DUSDP second "steam pass" in June and July 1993.

For the direct treatment of vapor, Continental Recovery Systems (CRS) of Natick, Massachusetts, designed and built a self-regenerating GAC adsorption system for LLNL. One of two 340-kg (750 lb) GAC vessels is used to adsorb extracted vapor while the other vessel, which will have been saturated by prior use, is desorbed using the unit's 100 kW (400,000 BTU/h) steam generator. Regenerated vapor, consisting almost entirely of steam and gasoline vapor, is condensed in a small flat-plate heat exchanger and separated in an OWS within the unit. This system can collect about 100 L (30 gals) of gasoline per day.

Hydrocarbon concentrations in the extracted vapor increased from around 2,500 ppmv total hydrocarbons (TH), measured in early February 1993, to as high as 100,000 ppmv TH in April 1993, after the DUSDP first steam injection phase. To increase the gasoline removal capacity above the CRS trailer's 100-L (30 gal)/d limit, we installed a VR Systems ICE capable of extracting and burning as much as 600 L (150 gals) of gasoline per day. The stand-alone unit consists of two 7.5-L (460 in.^{3}) displacement Ford industrial engines controlled by a microprocessor. The unit automatically blends dilution air into extracted vapor to maintain excess oxygen in the exhaust's catalytic converters.
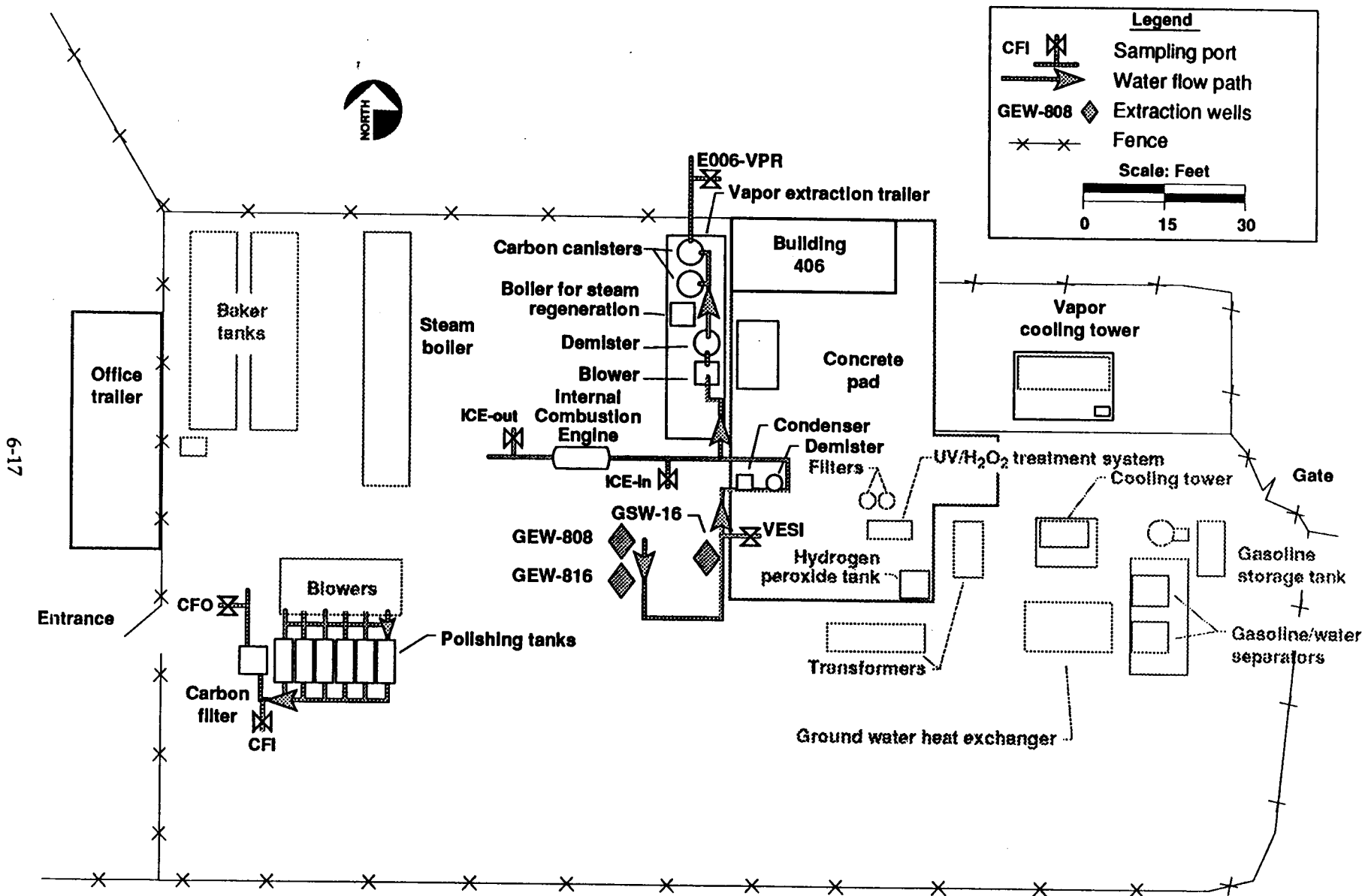
Legend

CFI — Sampling port

Water flow path

GEW-808 ◈ Extraction wells

✕—✕ Fence

Scale: Feet

0   15   30

NORTH

E006-VPR

Vapor extraction trailer

Carbon canisters

Boiler for steam regeneration

Demister

Blower

Internal Combustion Engine

ICE-out

ICE-In

Baker tanks

Office trailer

Steam boiler

Building 406

Concrete pad

Vapor cooling tower

Condenser

Demister

Filters

UV/H_2O_2 treatment system

Cooling tower

Gate

GSW-16

GEW-808

GEW-816

VESI

Hydrogen peroxide tank

Gasoline storage tank

Gasoline/water separators

CFO

Entrance

Blowers

Polishing tanks

Carbon filter

CFI

Transformers

Ground water heat exchanger

Figure 3. TFF vapor treatment.

Both the vapor and water treatment systems at TFF are operated and controlled by an IBM-type 486-microprocessor-based computer. Although the facility typically operates near steady-state, many operational parameters are monitored by the computer. If any of the parameters fall out of the planned normal range, the computer is capable of shutting down the entire system and alerting an operator. The controlling computer also allows automatic data-logging of process parameters.

Extraction Operations, September 1 to November 12, 1993

During September 1993, vapor and water extraction and treatment were carried out on a one-shift-per-day basis for 12 days, with a total operating time of 78 h. Daily hours of operation ranged from 5 to 8 and averaged 6.5. Approximately 174,000 gal of water and 840,000 ft^3 of vapor were removed and treated at the TFF site. This corresponds to removal rates of 34 gal/min and 165 scfm, respectively. Initial concentration of THs, as measured at the input to the ICE where the gasoline vapors are destroyed, was 21 mg/L (6,000 ppmv at STP) on September 1. The last ICE measurement for the month, taken on September 22, was 17 mg/L (4,800 ppmv). Concentrations of THs in the water averaged about 18,000 ppb. A total of 26 gal of gasoline was recovered from the pumped water, 19 gal as condensate, and 167 gal were destroyed or recovered from the vapor extraction for a total removal of 212 gal.

Three-shift, 24-h, 7-days-per-week operation of the water pumping and treatment system and the ICE vapor extraction/destruction system commenced on October 4, 1993 (Julian day 277). Water pumping throughout the entire ARV phase came from the three central extraction wells, GEW808, GEW816, and GSW16 (Fig. 1). Initially, vapor extraction was carried out from these same wells from screened intervals covering a large portion of the vadose zone between 20 ft and the top of the water level in the well, which ranged from 102 to 122 ft in depth. Average extraction rates were about 100 scfm for vapor and about 50 gal/min for water. As seen in Figure 4, initial concentrations of THs, sampled at the input to the ICE, were 16 to 19 mg/L (4,500 to 5,400 ppmv). These levels decreased rapidly to about 7 to 9 mg/L (2,000 to 2,500 ppmv) during the next 2 weeks of operation.

The initial hydrocarbon concentration of 18 mg/L (5,200 ppmv), at 100 scfm extraction rate, means that about 26 gal/d were being destroyed. As the concentration dropped to half of this level, 9 mg/L (2,600 ppmv), we were recovering about 13 gal/d. At these relatively low rates, we were not using the ICE very efficiently as a recovery/destruction system. In addition, because of the wide depth range of screened intervals in the extraction wells, we knew we were not focusing the flow of vapor into the most highly contaminated parts of the vadose zone. The injection wells have screened intervals confined to the upper steam zone of the vadose zone. We, therefore, decided to try to increase the recovery rates by shifting the vapor extraction to several of the injection wells (GIW813, GIW815, GIW818, and GIW820) shown in Figure 1, which had good vapor flow characteristics.

Initially, GEW808 and GEW816 were taken out of the vacuum stream and GSW16 was left in when the injection wells were connected to the ICE on October 18 (day 291). Vapor in the injection wells was extracted from a 20-ft screened interval in the upper steam zone aquifer, located in the vadose zone at depths of 67 to 105 ft (different for each well). As seen in Figure 4, initial concentrations for the composite of all these wells, as measured at the input to the ICE,
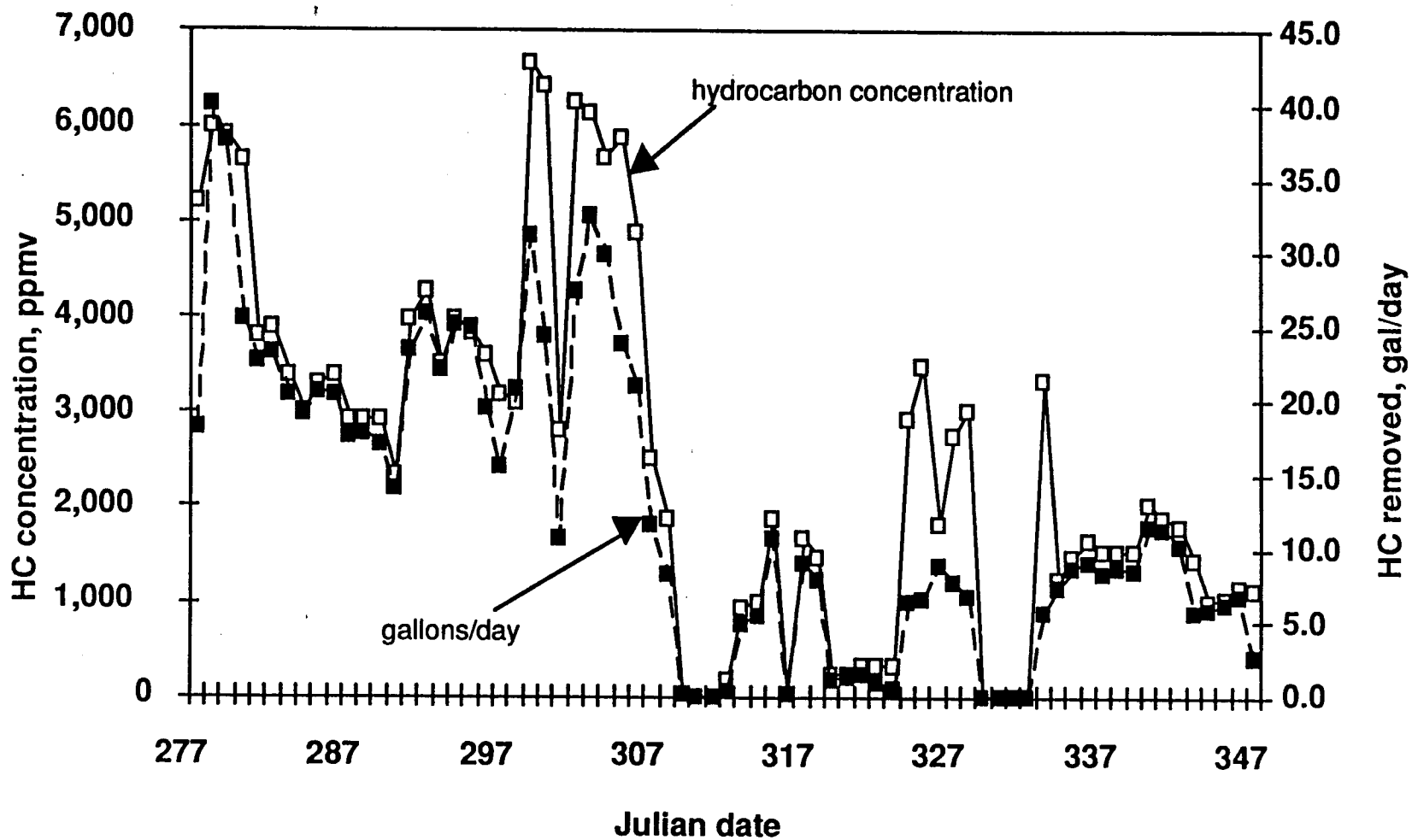
Figure 4. Concentration of total hydrocarbons (mg/L), measured at the input to the ICE, and daily hydrocarbon removal rate in gallons/d (a function of concentration and flow rate) versus elapsed time in days for the ARV project.

went up to 10 or 11 mg/L (about 4,000 ppmv). There was a considerable dilution effect from the lower concentrations in GSW16; this was revealed when we took GSW16 off-line on October 26 (day 299), and concentrations at the ICE input (Fig. 4) jumped back up to 18 mg/L (6,600 ppmv) when we were only extracting from the four injection wells. Coincident with the jump in concentration was a drop in the rate of vapor flow by about one-third from the four injection wells (about 120,000 scf/d) compared to the previous case when GSW16 was included (about 180,000 scf/d). Apparently, about one-third of the flow in the vapor system had been coming from GSW16.

Contaminant levels in each of the four injection wells were measured on October 21 (day 294) and again (after GSW16 was isolated) on October 28. Results are shown in Table 1. A flow test completed on October 28 (day 301) on each of the four injection wells revealed that about 50% of the flow was coming from GIW815, with the rest equally divided (at 16 to 17% each) between the other three wells. Partitioning the concentrations for October 28 according to the flow distribution gives a total concentration in the flow of 6,360 ppmv. This number agrees well with average concentrations of the composite flow measured at the input to the ICE for that general time period.

Vapor extraction continued from the injection wells until November 5 (day 309) when the entire TFF system was shut down in preparation for a weekend power outage. As seen in Figure 4, concentration levels declined gradually between October 18 and November 5. In preparation for the air sparging operations (described in Section III), on November 8 (day 312) we returned to extraction from the three central extraction wells after the power outage. We expected that hydrocarbon concentrations at the input to the ICE upon resumption of extraction from these wells would be comparable to or higher than the values measured on October 17, prior to switching to extraction from the injection wells. Instead, concentration levels (Fig. 4) were much lower, in the range of 1,000 ppmv or less instead of the expected 3,000 to 4,000 ppmv. It is likely that these values were anomalously low because of sampling problems (Section III and Appendix 4). This phase of operations ended on November 16 (day 320) with the beginning of air sparging operations, described in the next section. In addition to changes in hydrocarbon concentrations, operations from October 4 to November 11 affected the level of the water table and subsurface temperatures under TFF; these changes are described below.

Table 1. Composition of hydrocarbon vapor samples of injection wells.

| | Total petroleum hydrocarbon content in vapor | | | |
| | October 21, 1993 | | October 28, 1993 | |
Well ID	TPH (mg/L air)	TPH (ppmv)	TPH (mg/L air)	TPH (ppmv)
GIW-813	44.0	12,580	49.6	13,840
GIW-815	13.0	3,670	15.3	4,270
GIW-818	7.7	2,190	18.8	5,250
GIW-820	32.0	9,010	22.0	6,130

Temperatures were measured throughout the TFF site at different depths from a network of thermocouples installed for the DUSDP. These thermocouples were continuously monitored by the data acquisition system throughout the ARV phase. From these data, we estimated the subsurface thermal conditions at the site, and their changes over time. In addition, continuous measurements of water level were made in the extraction wells, where the pumps were operated continuously, and daily water level measurements were made in seven surrounding wells. From these data, we more precisely monitored changes in the water table (or hydraulic head) that resulted from pumping at rates that averaged 50 gal/min (72,000 gal/d).

Figure 5 shows in plan view the temperature distribution on October 5 at the depth of the upper steam zone (80-ft or 24.4-m depth). This is the area most strongly affected by steam injection during DUSDP activities in March through July. Monitoring well TEP010, which is at a temperature of 96.5°C (206°F) at the 24.4-m depth, is located close to the extraction wells and in the center of the steam injection ring used in the DUSDP project. The temperature distribution was controlled by the steam injection process and lithology. Permeable zones through which most of the steam passed were heated to near boiling temperatures, while less permeable zones, mainly above and below the level shown in Figure 5, remained cool. This can be better seen in the cross section in Figure 6, which shows that the highest temperatures were confined to levels between 70 ft (21.3 m) and 120 ft (36.6 m). This encompasses the upper and lower steam zones. Note that by October, 3 months after the end of steam injection, underground temperatures were still high and the clay aquitard layer, which is at a depth of about 100 to 115 ft (30.5 to 35 m), had been heated by conduction to temperatures similar to those in the upper and lower steam zones. Aside from changes associated with ground water flow, the temperatures shown in Figures 6 and 7 decreased by only by 1° to 2°C during the entire ARV phase.

Water levels measured in the five wells at the TFF site during the ARV phase are shown in Figure 7. The trends are complicated by various system configuration changes that were made throughout the course of the project, but the decline curve due to pumping during the first 2 weeks, while vacuum was simultaneously applied to the wells where water pumping was occurring, is readily seen. As expected, water levels dropped by 2 to 3 ft when vacuum was shut off in the extraction wells (around Julian day 291) because of the increased air pressure in the wells. Figure 8 shows the configuration of the water table (since the water is being pumped from the lower steam zone aquifer, it more accurately represents a surface of constant head in the lower steam zone) under the TFF site after 21 days of continuous pumping (on October 25). The original water table was at the 102- to 104-ft (31.1- to 31.7-m) depth; in Figure 8, the water table is at depths greater than 112 ft (34.1 m) over a large area. Note also the cone of depression around the extraction wells. This cone is not symmetric; it is flattened on the western side probably due to permeability variations. More closely spaced water level contours occur in areas of lower permeability; this suggests that most of the flow in the lower aquifer is from the southeast. Note that this flow direction also corresponds to the axis of elongation of the 95°C contour in Figure 5; this is because the temperatures are controlled by preferential paths for steam, which follow the direction of maximum permeability. The real significance of Figure 8 is that it shows that we were successful in drawing the water table to depths within or below the depth of the clay aquitard, which was the target zone for enhanced contaminant recovery.
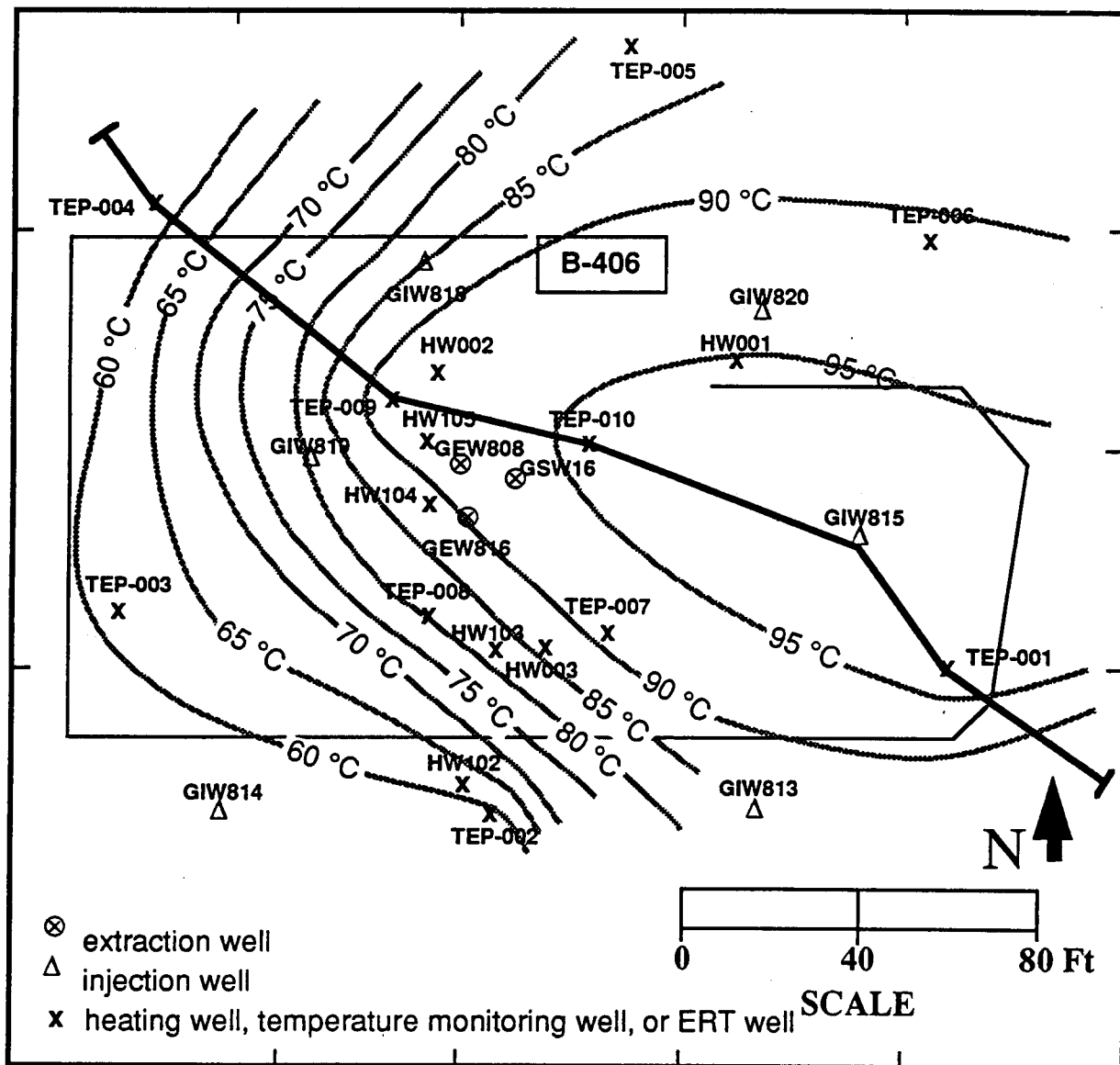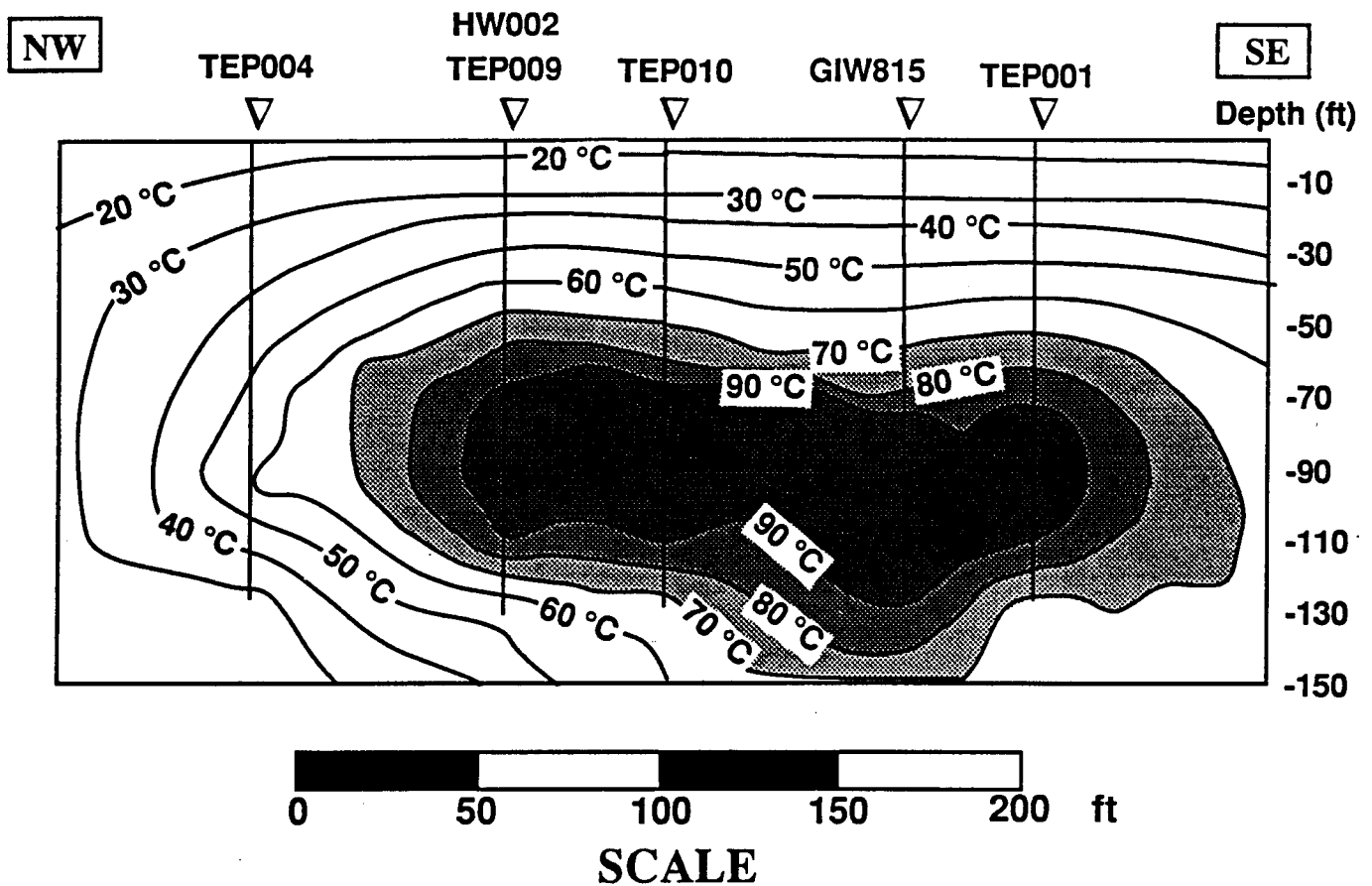
Figure 5. Plan view of temperature distribution in the upper steam zone (80-ft or 24.4-m depth) at the beginning of ARV operations on October 5, 1993. Well symbols are the same as those used in Figure 1. This is the zone most strongly heated by steam injection during the DUSDP. The line of section shows the location of the cross section shown in Figure 6.

Figure 6. Cross section (see Fig. 5 for section line) showing temperature distribution at the TFF site at the beginning of October 1993. Well locations with data control points are indicated. Note the zone of high temperatures at the 70- to 130-ft depth (the location of the upper and lower steam zones and the clay aquitard) affected by steam during the DUSDP.
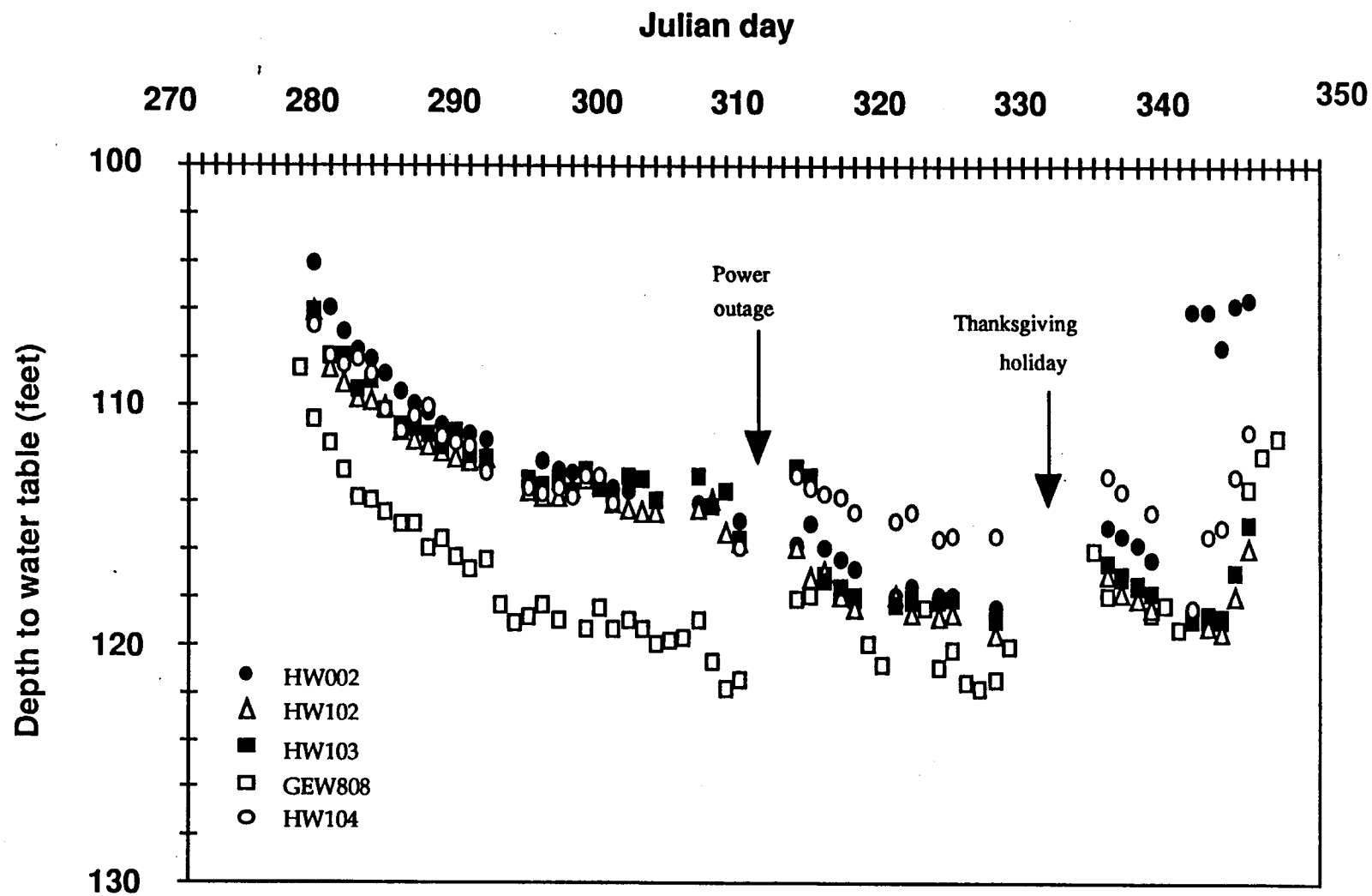
Figure 7. Water levels in selected wells versus time during ARV operations. Well locations are shown in Figure 1.
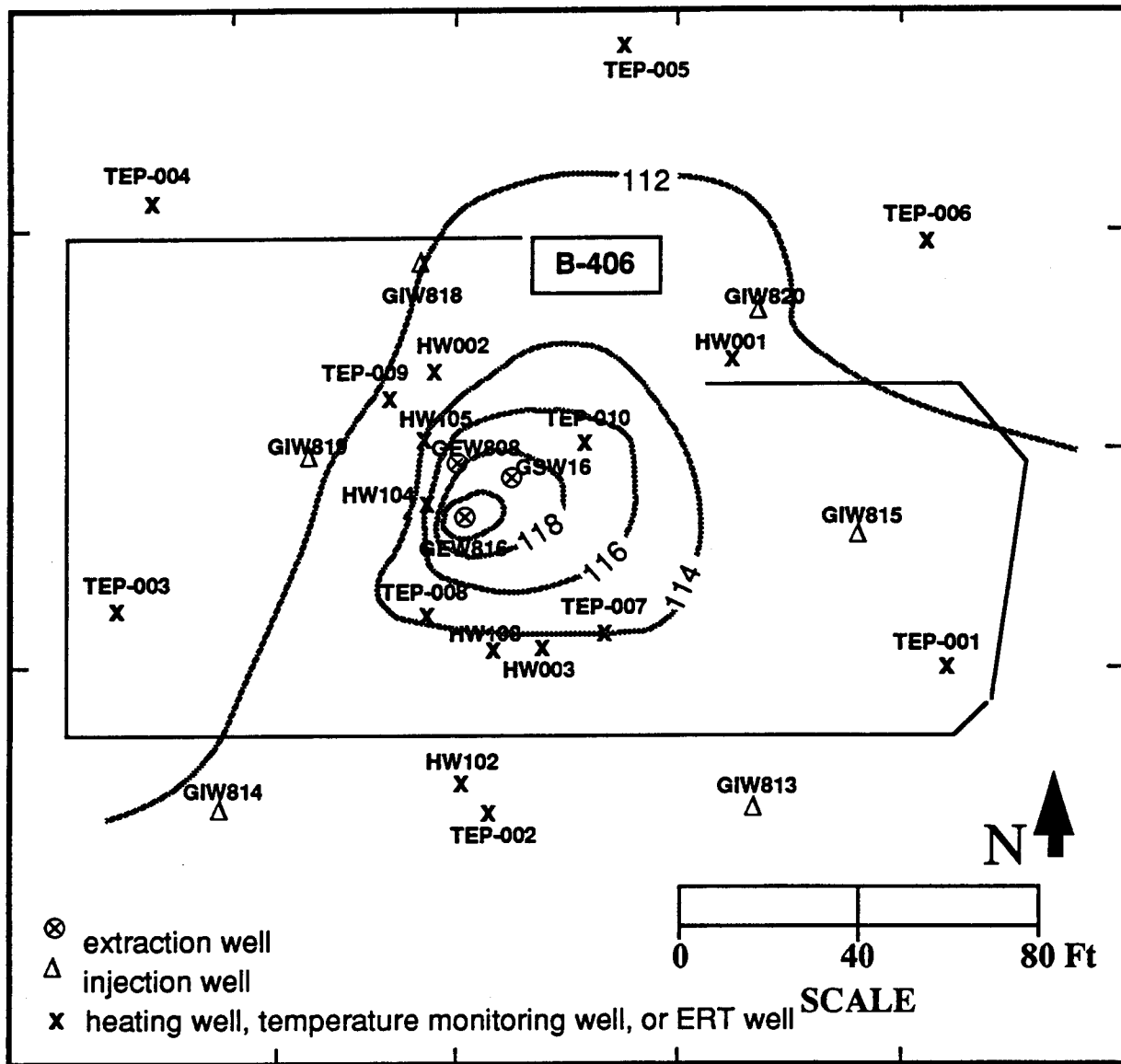
Figure 8. Plan view of the water table at the TFF site as measured on October 25, 1993, after 21 days of continuous pumping of ground water at about 50 gal/min from the central extraction wells (located at the center of the cone of depression). Contours are in feet below the surface. The background water level before pumping began was about 102 to 104 ft deep.

However, as stated above, the water levels are more indicative of head in the lower aquifer and do not imply significant drainage of the clay zone.

Pumping water draws in a significant volume of water from outside the area that had been affected by steam and would therefore be expected to cool the formation. This has in fact been observed, as seen in Figure 9, which shows the difference in temperature of the lower steam zone (130-ft or 39.6-m depth) between October 4, before 24-h pumping began, and October 28, after 23 d of continuous pumping. The greatest amount of cooling occurs to the west of the central extraction wells, where only about 2°C of cooling has occurred. Figure 9 shows that cooler water is obviously flowing into the TFF area from the south along a relatively narrow zone that is probably controlled by the local permeability. We also note that these dramatic cooling effects are *not* seen at other depths below TFF; this effect is confined to the lower steam zone aquifer, the zone that is being pumped. When Figure 9 is compared with Figure 10, which shows differences in temperatures between September 15 and October 4 (before we started continuous pumping of ground water), one can see the dramatic effect of ground water withdrawal on the subsurface temperatures.
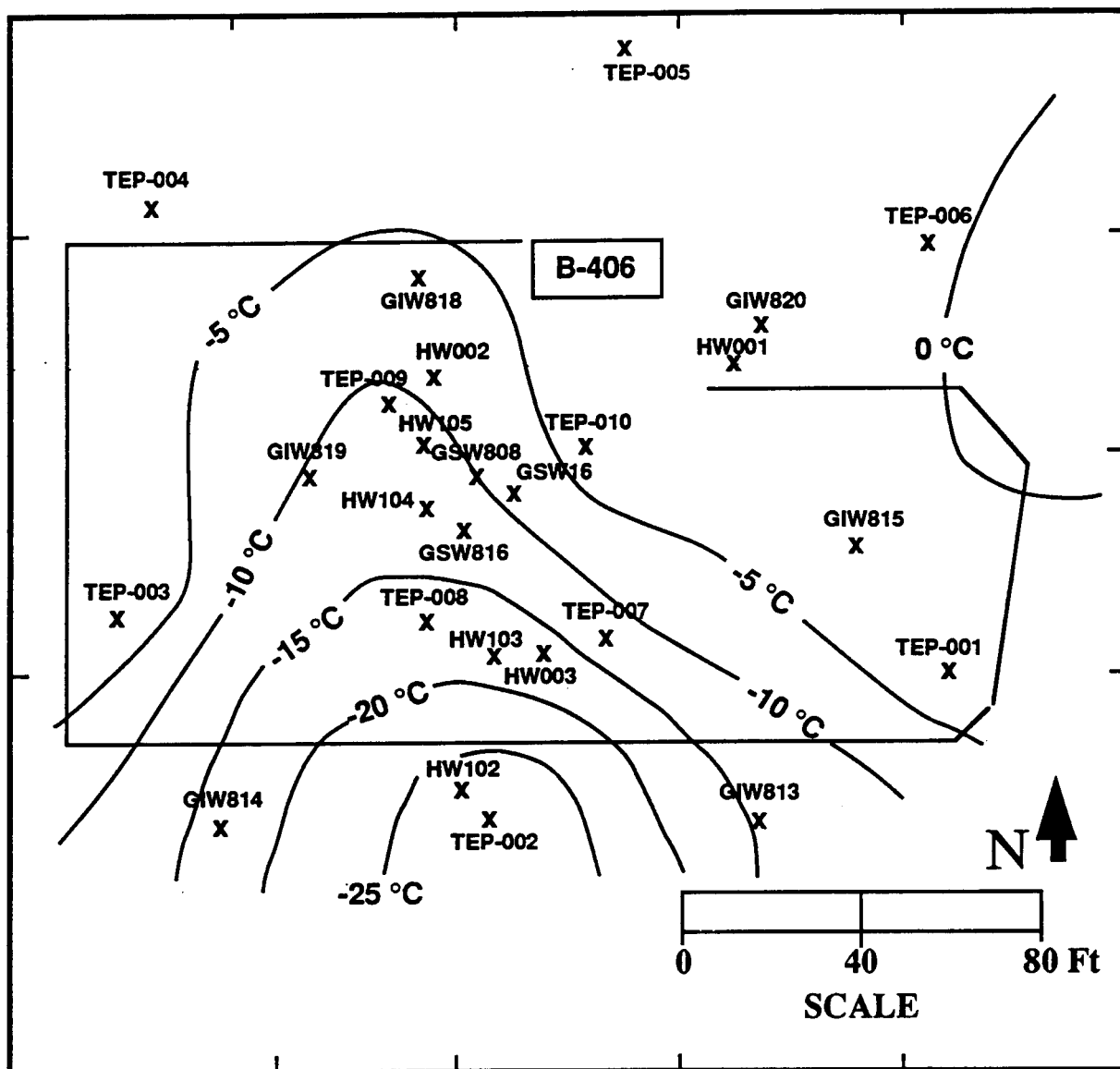
Figure 9. Plan view at the TFF site of the difference between October 4, 1993, and October 28, 1993, in the temperature at the 130-ft (39.6-m) depth, the depth of the lower steam zone. Temperature differences in degrees Celsius. Note the large zone of lowered temperatures due to the influx, within the lower steam zone aquifer, of cold water from the southern boundary of the site.
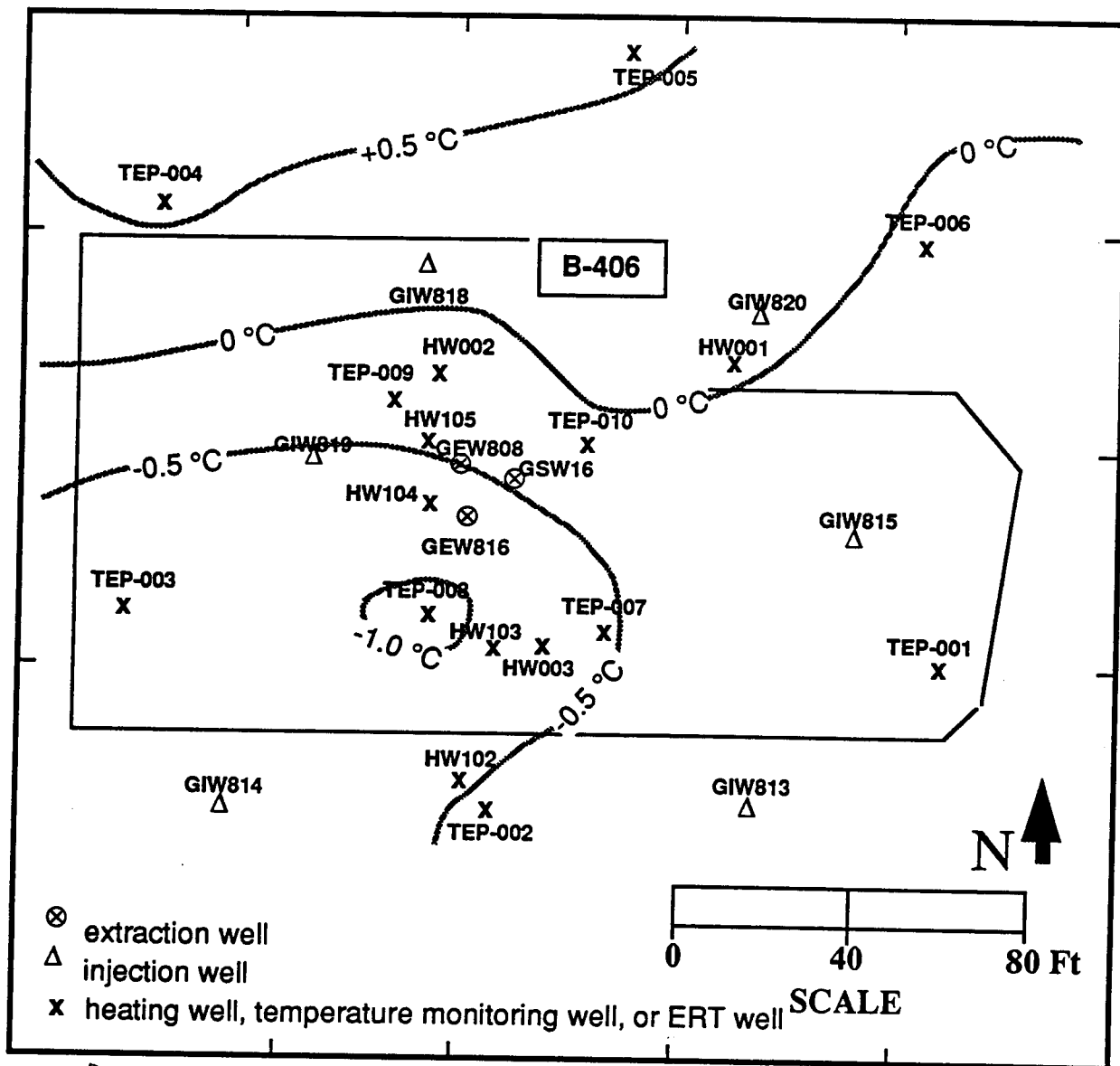
Figure 10. View similar to Figure 9, except that the difference in temperatures is between September 15, 1993, and October 4, 1993, when 24-h pumping of ground water was not taking place. Note the lack of perturbation of subsurface temperatures in the lower steam zone.